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Radiological hazards of TENORM in precipitated calcium carbonate generated as waste at nitrophosphate fertilizer plant in Pakistan

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ABSTRACT

The NORM (naturally occurring radioactive material) in phosphate rock is transferred as TENORM (technologically enhanced naturally occurring radioactive material) to phosphatic fertilizers and to the waste generated by the chemical processes. The waste generated at the NP (nitrophosphate) fertilizer plant at Multan in Pakistan is PCC (precipitated calcium carbonate). Thirty samples of the PCC were collected from the heaps of the waste near the fertilizer plant. Activity concentrations of radionuclides in the waste samples were measured by using the technique of gamma ray spectrometry consisting of coaxial type HPGe (high purity germanium) detector coupled with a PC (personal computer) based MCA (multichannel analyzer) through a spectroscopy amplifier. Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the waste samples were determined to be 273 ± 23 (173–398), 32 ± 4 (26–39) and 56 ± 5 (46–66) Bq kg^{-1} respectively. The activity concentration of ^{226}Ra in the PCC waste was found to be higher than that in naturally occurring calcium carbonate (limestone and marble) and in worldwide soil. Radiological hazard was estimated from indoor and outdoor exposure to gamma rays from the PCC. Indoor annual effective dose was higher than 1 m Sv. Potential radiological pollution in the environment from TENORM in the PCC has also been addressed.

1. Introduction

Phosphate rock (PR) of sedimentary origin exists in the earth's crust in the form of calcium phosphates $Ca_3(PO_4)_2$ [1] and the rock contains NORM (naturally occurring radioactive material). Generally the NORM is composed of radionuclides of uranium and thorium series, and their progeny [2]. In phosphate rocks, the NORM is mainly of uranium series that dominates due to the replacement of Ca^{+2} by U^{+4} in $Ca_3(PO_4)_2$ [3]. While making fertilizers from PR, the NORM is converted into TENORM (technologically enhanced naturally occurring radioactive material) in the product material and in the process generated waste. Whenever uranium or thorium bearing minerals are exploited, NORM containing by – products and TENORM contaminated wastes are created [4,5]. The elevated radionuclide concentrations are the result of chemical or physical processes taking place during (re-) processing of raw materials. The TENORM is found in the waste streams of phosphate industry [6,7]. Phosphogypsum (PG) is a common form of the generated waste (when PR is dissolved in H_2SO_4 to produced H_3PO_4) at many PF (phosphate fertilizer) industries in the world and the waste is contaminated with the TENORM [7]. When PR is dissolved in HNO_3, the radionuclides in the rock are leached by the acid and become part of the process solution. The crystallized or precipitated calcium carbonate (PCC) waste of NP (nitrophosphate) fertilizer plant is contaminated by the process solution containing radioactivity in proportion to that was in the PR [8].

In Pakistan, the NP fertilizer is made at Pak-Arab factory in Multan. Sedimentary PR is imported from Jordan and Morocco. The fertilizer is produced by dissolving the PR in HNO_3. A mixture of H_3PO_4 and $Ca(NO_3)_2$ is produced. The mixture is cooled to below 0 °C, where the $Ca(NO_3)_2$ crystallises and is separated from the H_3PO_4. The $Ca(NO_3)_2$ is converted into NH_4NO_3 and $CaCO_3$ using CO_2 and NH_3. The solution is filtered and $CaCO_3$ (precipitated calcium carbonate) crystals are removed as process waste. The solution of NH_4NO_3 is concentrated to produce NH_4NO_3 fertilizer. The solution from which the PCC is removed is processed to obtain the NP fertilizer [9,10]. The Pak-Arab fertilizer factory has the capacity to process 550 tones of PR daily. Around 45% of the processed PR is converted to the PCC.

The PCC waste is kept in a trench in the vicinity of the Pak-Arab fertilizer factory for interim storage to dry in the sun for reducing the moisture content, the material is then removed from the transitory stockpile to make vacancy for the new waste. There are many options for the management of the PCC waste; such as disposal or dumping, stacking, use-in agriculture, apply in construction (production of bricks, cement, paint, etc.) or landfill [11]. The PCC waste

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generated through chemical processes becomes radioactively contaminated due to the enhanced concentration of ^{226}Ra (the decay product of ^{238}U series) and its progeny in the waste.

As far as disposal of the process waste of NP industry is concerned, it is especially hazardous if the PCC waste containing TENORM is used in the construction of houses. The PCC with TENORM in the building material becomes a source of external exposure to gamma rays and internal exposure to alpha particles of radon [12]. Radon accumulates in the house due to the presence of radium in the PCC waste. In addition to construction applications, calcium carbonate has many other applications in industry, agriculture, health, environment, etc. The TENORM in the PCC of NP fertilizer factory is potential source for dispersion of radioactivity in the environment.

The importance for the assessment of the TENORM in usable materials has increased because the risk from low level chronic radiation is very serious [13]. Besides the fact that many papers have been devoted to the radiological impact of PG [6,7,14], but reference data for radioactivity contained in the PCC waste of NP fertilizer plant is limited [2,8]. The present study was therefore performed to measure activity concentration of radionuclides in the samples of PCC waste generated at the NP fertilizer factory at Multan in Pakistan. This is the first study that was carried out on the PCC generated in Pakistan. Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were determined by an HPGe based gamma ray spectrometry system. The associated radiation hazard in terms of radiation dose was derived from the measured activity concentrations of the radionuclides in the waste material. Potential radioactive pollution of the waste has also been addressed in this paper.

2. Materials and methods

2.1. Sampling and sample preparation

The sampling of the PCC waste was carried out in 5 batches. Each batch consisted of 6 samples and the total number of samples were therefore 30. The samples of every batch were collected after an interval of at least 2 months. For a representative sample, at least 5 specimens were collected such that a central specimen was surrounded by at least 4 specimens acquired at a radius of about 2 m. The specimens were mixed homogeneously and at least 2 kg of the material was taken as one sample. The samples were properly catalogued and brought to the laboratory to prepare for gamma spectrometry. The samples were first dried in the sun then in a microprocessor controlled furnace at 110 °C for 24 h. The material was passed through a sieve of 30 μm mesh size. The powder was packed in Marinelli beakers of about 1 L volume. IAEA reference materials, RGU-1, RGTh-1 RGK-1 of known activity concentrations were also packed in the Marinelli beakers. The samples and reference materials were properly sealed to control leakage of radon, and stored for about 2 months to achieve secular equilibrium between ^{226}Ra and ^{222}Rn. More details regarding sample preparation are given in references [15–17].

2.2. Determination of activity concentration

Activity concentrations of the radionuclides ^{226}Ra, ^{232}Th and ^{40}K in the samples of PCC waste were determined using the technique of gamma ray spectrometry. The measurement system consisted of coaxial type high purity germanium (HPGe) detector coupled with a PC based MCA through a spectroscopy amplifier. The detector was kept in a 30 cm × 30 cm × 30 cm cavity shielded with 10 cm lead with inner lining of copper, aluminium and Perspex. Resolution of the spectrometry system was 2.0 keV at 1332.5 keV energy. The spectra of the samples and reference material were collected and retained in the memory of the PC. Efficiency versus energy curve for the measurement system corresponding to the reference material was plotted and stored in the PC. The efficiency was used to calculate activity concentrations of the radionuclides in the samples of the PCC. Activity concentration of the PCC samples was further verified by comparison using the following relation:

$$A_S = \frac{m_R}{m_S} \times \frac{C_S}{C_R} \times \frac{t_R}{t_S} \times A_R \quad (1)$$

where the meanings of the symbols in the equation are as follows: S stands for sample, R for reference material, A for activity concentration, C for counts or net area under the peak, m for mass, and t for spectrum collection time. Microsoft Excel was applied to perform peak by peak activity calculations using Eq. (1). Activity concentration of ^{226}Ra was determined by averaging the activity concentrations of most abundant daughters in equilibrium with ^{226}Ra. Thorium-232 activity concentration was determined under the assumption that ^{232}Th was in equilibrium with its decay products (^{228}Ac, ^{212}Pb, ^{212}Bi, ^{208}Tl) during the chemical processing of phosphate rock for fertilizer production. The quality control of the measurements was checked by measuring activity concentration of the IAEA Soil-6. Details regarding activity concentration measurements of environmental samples are described somewhere else [18].

2.3. Assessment of radiological hazard

The hazard associated with radioactivity in a material is assessed through hazard indices. A hazard index is a parameter that is represented by a single value that takes into account the measured activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the material. Among the various types of hazard indices, the most common is the radiation absorbed dose.

Gamma absorbed dose rate in air at 1 m above the ground surface for the uniformly distributed naturally occurring radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in the ground is calculated based on guidelines provided by the UNSCEAR [19]. The outdoor absorbed dose rate $\dot{D}_{out}$ from external exposure to gamma rays at 1 m above the PCC ground was estimated by applying the following relation [19]:

$$\dot{D}_{out} = 0.462 \times A_{Ra} + 0.604 \times A_{Th} + 0.0417 \times A_K \quad (2)$$

The indoor absorbed dose rate $\dot{D}_{in}$ from external exposure to gamma rays at the centre of a room of 4 m × 5 m × 2.8 m dimensions constructed of radioactivity containing material, was calculated by using the relation given below [20]:

$$\dot{D}_{in} = 1.21 \times A_{Ra} + 1.29 \times A_{Th} + 0.10 \times A_K \quad (3)$$

where $\dot{D}_{out}$ and $\dot{D}_{in}$ are respectively the outdoor and indoor external dose rates (nGy h^{-1}), A_{Ra}, A_{Th} and A_K are respectively the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K (Bq kg^{-1}) in the materials of interest.

Annual effective dose from exposure to ionizing radiation was calculated using the following relation [19]:

$$E = \dot{D} \times T \times O \times f \times 10^{-6} \quad (4)$$

where E is the effective dose (m Sv y^{-1}), $\dot{D}$ is the absorbed dose rate (nGy h^{-1}), T is the time (8760 h y^{-1}), O is the occupancy factor, and f is the conversion factor (0.7 Gy Sv^{-1}). The substitution of the values of the quantities in Eq. (4), simplifies the above relation as given below:

$$E = 6.13 \times 10^{-3} \times O \times \dot{D} \quad (5)$$

According to the UNSCEAR report [19], the indoor and outdoor occupancy factors are 80% and 20% respectively. The substitution of

O as 20% and $\dot{D} = \dot{D}_{out}$ from Eq. (2) into (4) gives the outdoor annual effective dose:

$$E_{out} = [5.67A_{Ra} + 7.41A_{Th} + 0.51A_K] \times 10^{-4} \quad (6)$$

The substitution of O as 80% and $\dot{D} = \dot{D}_{in}$ from Eq. (3) into (4) gives the indoor annual effective dose:

$$E_{in} = [5.94A_{Ra} + 6.33A_{Th} + 0.49A_K] \times 10^{-3} \quad (7)$$

3. Results and discussion

3.1. Activity concentration

Activity concentrations of the radionuclides determined in the samples of PCC are given in Table 1. Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the PCC samples are 273 ± 23 (173–398), 32 ± 4 (26–39) and 56 ± 5 (46–66) Bq kg^{-1} respectively. Among the five batches of the waste samples, ^{226}Ra content differs between the batches. This is probably due to the different origin of PR in the various batches of the PR raw material imported for the production of NP fertilizer at Pak-Arab fertilizer factory. Activity concentrations of ^{232}Th and ^{40}K in PCC within statistical uncertainties are consistent from batch to batch.

Around 40% of the PCC generated at Pak-Arab NP factory in Pakistan is thrown as waste and 50% is used to make CAN (calcium ammonium nitrate) fertilizer; furthermore data on radioactivity in the PCC waste is scarce in literature. We could compile a few data on radioactivity from literature on solid waste from Brazil, Italy and Romania, where NP fertilizer is produced. The average activity concentration values are given in Table 2. Activity concentration of ^{226}Ra in Pakistani waste is comparable to that in Italian, whereas it is lower than that in Catalão-Brazilian and Romanian wastes, and it is higher than that in Tapira-Brazilian waste. As far as activity concentration of ^{232}Th in Pakistani waste is concerned, it is greater than that in Italian and Romanian wastes, whereas it is lower than that in Brazilian waste. Among the four countries in comparison, the activity concentration of ^{40}K in Pakistani PPC is similar with that from Romania but lower than that from other three countries.

Limestone, the sedimentary calcium carbonate (CC), and marble, the metamorphic CC, are the components of building materials. Both forms of CC come from the earth's crust therefore may contain natural radioactivity. Data on radionuclide activity concentration in limestone and marble was compiled for some countries of the world and is represented in Table 3. Activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in limestone is 11–76, 2–65 and 22–295 Bq kg^{-1} respectively, and that in marble is 0.5–23, 0.2–18 and 3.7–310 Bq kg^{-1} respectively. When compared with that for PCC waste of Pakistan, Brazil, Romania and Italy given in Table 2, it is clear that the natural radioactivity of limestone and marble are lower than that of the PPC produced in NP fertilizer industry. This is mainly due to the presence of ^{226}Ra in the process waste of NP fertilizer factories. The activity level of ^{226}Ra in the PCC is many fold higher than that in worldwide data on soil given in the UNSCEAR report [19] and represented in Table 3. The concentration of ^{232}Th is of the order of background level of worldwide soil [19] and that of ^{40}K is lower than the background.

The PR of Jordan and Morocco is used for the production of phosphatic fertilizers in several fertilizer factories in the world, therefore activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in these rocks have been measured by many investigators. Activity concentrations of the radionuclides in these rocks, compiled from literature are represented in Table 4. Activity concentration of the radionuclides in Moroccan PR is higher than that in Jordanian PR. Radium-226, a daughter product of ^{238}U decay series, is the main contributor of natural radioactivity content in PR (due to the replacement of calcium ions by uranium ions in PR). Activity concentration of ^{226}Ra in Jordanian and Moroccan PR varies in ranges 681–1044 and 1200–1700 Bq kg^{-1} respectively. The contribution of ^{232}Th and ^{40}K is very small, therefore not of much significance. The larger value of ^{226}Ra activity in PR is distributed between the PF and the waste generated by the PF plants.

Most of the fertilizer manufacturing factories in the world produce H_3PO_4 by dissolving PR in H_2SO_4 and generate PG as waste. Some of the factories produce phosphate fertilizers by dissolving PR in HNO_3 and create PCC as waste. Data on activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in PF produced by dissolving PR in H_2SO_4 and HNO_3, and that in the resulting PG and PCC have been compiled in Tables 2 and 5–7 for some fertilizer plants in the world. The content of these radionuclides in Pakistani fertilizer (Table 5) are higher than that in the Italian and Romanian fertilizers, and also than that in the understudy PCC waste.

Activity concentration of ^{226}Ra in PG varies in range 106–740 Bq kg^{-1} that in PCC varies in range 173–398 Bq kg^{-1}. The concentration of this radionuclide in PF produced by dissolving PR in H_2SO_4 varies in range 5–366 Bq kg^{-1} and that produced by dissolving PR in HNO_3 varies in range 124–501 Bq kg^{-1}. There is a large variation in activity concentrations of the radionuclides in the industrial product PF, and the wastes PG and PCC. In both of the processes of PF production (via H_2SO_4 or HNO_3), the product (fertilizer) and wastes (PCC and PG) contain a significant amount of TENORM [21]. The PG is a big waste management problem and the disposal of PCC is also a great trouble.

3.2. Radiological hazard

Eqs. (2) and (3) involve activity concentrations of all the three radionuclides, therefore outdoor and indoor external dose rates fall under the definition of hazard indices. It was assumed that the contributions from other naturally occurring radionuclides, such as ^{235}U, ^{87}Rb, ^{138}La, ^{147}Sm and ^{178}Lu, to actual dose rates were insignificant.

3.2.1. Outdoor external dose

From the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K measured in the waste samples, $\dot{D}_{out}$ as radiological hazard of PCC was calculated using Eq. (2) and is given in Table 1. The average value and range of $\dot{D}_{out}$ from the PCC is 148 ± 32 (103–207) nGy h^{-1}. The average value is about three times greater than the background median value of absorbed dose of gamma rays from worldwide soil given in Table 3. The mean values of $\dot{D}_{out}$ of the waste generated by Batchs 2 and 3 were even greater than the overall mean value.

The mean values of $\dot{D}_{out}$ for the Brazilian, Italian and Rumanian waste samples given in Table 2 are greater than that for the Pakistani waste. The range values of $\dot{D}_{out}$ for limestone and marble given in Table 3 are 7–71 and 2–34 nGy h^{-1} respectively, which are smaller than that for the understudy PCC waste. Radiological hazards of the PCC waste and NP fertilizer produced at Pak-Arab factory in Pakistan are given in Tables 1 and 5, respectively. The values of the radiological risk to the PCC and NP are of the same order of magnitude and only slightly higher for NP. The value of $\dot{D}_{out}$ from PG data given in Tables 6 and 7 is 125–349 nGy h^{-1}, which is higher than that from the understudy PCC.

An occupational worker may spend 2000 out of 8760 h (~20%) in a year on the waste of NP fertilizer plant. For 20% occupancy factor, annual effective dose was calculated using Eq. (6) and the E_{out} is 0.18 ± 0.04 (0.13–0.25) m Sv. The worldwide average of the E_{out} from soil is 0.07 m Sv [19]. The effective dose from the PCC is therefore 2–3 times higher than that of worldwide soil, but it does not exceed the annual limit of 20 m Sv for an occupational worker and even the limit of 1 m Sv for general public as recommended by the ICRP [22]. The outdoor occupancy factor is smaller than 20%

Table 1
Activity concentrations of radionuclides in, and associated dose rates from PCC waste samples collected from NP fertilizer factory at Multan, Pakistan.

Sample	Activity concentration (Bq kg^{-1})			Dose rate (nGy h^{-1})		Effective dose (m Sv y^{-1})	
	^{226}Ra	^{232}Th	^{40}K	$\dot{D}_{out}$	$\dot{D}_{in}$	E_{out}	E_{in}
Batch 1							
W-1	223 ± 21	27 ± 4	58 ± 6	122	232	0.15	1.14
W-2	247 ± 22	30 ± 4	55 ± 6	134	239	0.16	1.17
W-3	257 ± 22	30 ± 4	60 ± 6	139	241	0.17	1.18
W-4	245 ± 22	36 ± 5	63 ± 6	137	240	0.17	1.18
W-5	276 ± 23	30 ± 4	46 ± 5	148	246	0.18	1.21
W-6	230 ± 21	26 ± 4	66 ± 7	124	234	0.15	1.15
Batch 2							
W-7	394 ± 28	28 ± 4	53 ± 6	201	274	0.25	1.34
W-8	304 ± 24	27 ± 4	47 ± 6	159	252	0.19	1.24
W-9	379 ± 27	38 ± 5	54 ± 6	201	273	0.25	1.34
W-10	364 ± 27	35 ± 5	50 ± 6	191	268	0.23	1.32
W-11	276 ± 23	29 ± 4	61 ± 6	147	246	0.18	1.21
W-12	398 ± 28	35 ± 5	51 ± 6	207	277	0.25	1.36
Batch 3							
W-13	377 ± 27	31 ± 5	58 ± 6	195	271	0.24	1.33
W-14	284 ± 24	39 ± 5	55 ± 6	157	250	0.19	1.23
W-15	374 ± 27	35 ± 4	47 ± 5	196	271	0.24	1.33
W-16	350 ± 26	30 ± 4	57 ± 6	182	264	0.22	1.29
W-17	350 ± 26	32 ± 4	63 ± 6	184	265	0.23	1.30
W-18	293 ± 24	29 ± 4	58 ± 6	155	250	0.19	1.23
Batch 4							
W-19	200 ± 20	39 ± 5	56 ± 6	118	230	0.15	1.13
W-20	201 ± 20	30 ± 4	51 ± 6	115	229	0.14	1.12
W-21	201 ± 19	29 ± 4	62 ± 6	113	228	0.14	1.12
W-22	203 ± 19	30 ± 4	57 ± 6	114	228	0.14	1.12
W-23	173 ± 18	35 ± 5	54 ± 5	103	222	0.13	1.09
W-24	187 ± 19	39 ± 5	52 ± 5	112	227	0.14	1.11
Batch 5							
W-25	222 ± 21	31 ± 4	65 ± 7	124	233	0.15	1.14
W-26	238 ± 22	26 ± 4	60 ± 6	129	236	0.16	1.16
W-27	200 ± 20	33 ± 4	58 ± 6	115	229	0.14	1.12
W-28	248 ± 22	36 ± 5	52 ± 6	138	241	0.17	1.18
W-29	236 ± 22	39 ± 5	49 ± 5	135	238	0.17	1.17
W-30	248 ± 22	33 ± 4	56 ± 6	137	240	0.17	1.18

for the general public, therefore the estimated dose is lower (in proportion to the occupancy factor) than that mentioned above.

Calcium carbonate is applied in agriculture fields because it is the principal source of calcium, an essential element for the growth of plants, and acts as a soil amendment that improves soil structure and reduces acidity. Calcium aids root development and helps the formation of healthy root cell walls; the transportation of carbohydrates and water, and the production of healthy seeds, and promotes biological activity in the soil. Acidic soil is a major limiting factor in achieving sustainable food production. Being alkaline, the PCC waste is used to reduce the acidity of agricultural field [23]. Although the soil to plant transfer factor depends on the various factors such as bioavailability, leachability, oxidation state, pH, electrical conductivity, soil texture, bicarbonate, carbonate, sulfate content of soil [24], the presence of TENORM in PCC may contaminate not only the soil but also the crops due to the uptake and therefore human beings can be directly or indirectly exposed to this radioactivity. Annual effective external dose from the PCC used for soil amendment and levelling depends not only on its amount but also its thickness in soil surface. The mixing of PCC dilutes its concentration in soil, and hence lowers the dose than that estimated for PCC only. About 8% of the PCC generated at the understudy factory is utilized by the agriculture sector.

3.2.2. Indoor external dose

The PCC discarded as waste (40% of the total PCC) is free to be used for any purpose; a fraction is utilized in construction industry in the adjoining areas of the Pak-Arab factory at Multan, Pakistan, where it is used for land filling and for house construction. In house building, the PCC is used for the fabrication of bricks, calcinations in

Table 2
Activity concentrations of radionuclides in, and associated external dose rates from PCC waste from some NP fertilizer industries of the world and that from the present study.

Country	Activity concentration (Bq kg^{-1})			Dose rate (nGy h^{-1})	Reference
	^{226}Ra	^{232}Th	^{40}K	$\dot{D}_{out}$	
Pakistan					
Mean	273 ± 23	32 ± 4	56 ± 6	148	Present study
Minimum	173 ± 18	26 ± 4	46 ± 5	103	
Maximum	398 ± 28	39 ± 5	66 ± 7	207	
Brazil/Tapira	195	579	504	460.82	[6]
Brazil/Tapira	214	631	532	502.18	[6]
Brazil/Catalão	364	989	276	777.03	[6]
Brazil/Catalão	292	1081	255	798.46	[6]
Italy	270	6.7	1200	178.83	[8]
Romania	350	8.12	63.99	169.27	[2]

Table 3
Activity concentrations of radionuclides in, and associated external dose rates from limestone, marble, and soil from different countries of the world.

Country	Activity concentration (Bq kg^{-1})			Dose rate (nGy h^{-1})	Reference
	^{226}Ra	^{232}Th	^{40}K	$\dot{D}_{out}$	
Limestone					
Algeria	16 ± 3	13 ± 2	36 ± 3	16.75	[34]
China	19.5 ± 2.8	13.4 ± 3.7	63.2 ± 5.4	19.74	[35]
China	21.5 ± 8.3	15.4 ± 3.6	83.2 ± 15.4	22.70	[36]
Egypt	45 ± 7	61 ± 8	198 ± 14	65.89	[37]
Israel	12.1	4.1	51.1	10.20	[38]
Israel	18.3	4.4	77.1	14.33	[38]
Italy	65 ± 5	6.1 ± 0.5	46 ± 4	35.63	[39]
Italy	76 ± 6	8 ± 0.7	47 ± 4	41.90	[39]
Nigeria	40.8 ± 23.1	65.2 ± 29.1	295 ± 120	70.53	[40]
Sicily	11 ± 8	2 ± 2	22 ± 33	7.21	[41]
Marble					
Algeria	23 ± 2	18 ± 2	310 ± 3	34.43	[34]
Cameroon	8 ± 2	0.35	19 ± 2	4.70	[42]
Egypt	11.8 ± 1	4.5 ± 0.6	18.8 ± 2.6	8.95	[43]
Italy	0.53 ± 0.08	3.9 ± 0.7	20 ± 3	3.43	[39]
Kuwait	3.9 ± 0.5	0.22 ± 0.08	3.7 ± 0.5	2.09	[44]
Malaysia	19 ± 3.4	16.5 ± 2.1	243.3 ± 49.3	28.89	[45]
Nigeria	2.4 ± 0.4	0.7 ± 0.2	6.6 ± 0.6	1.81	[40]
Pakistan	7.85 ± 7.02	2.74 ± 1.0	25.8 ± 42.8	6.36	[46]
Soil					
Worldwide					
Median	35	30	400	50.97	[19]
Minimum	17	11	140	20.34	
Maximum	60	64	850	101.82	

Table 4
Activity concentrations of radionuclides, and associated external dose rates from phosphate rock of Jordan and Morocco.

Country	Activity concentration (Bq kg^{-1})			Dose rate (nGy h^{-1})	Reference
	^{226}Ra	^{232}Th	^{40}K	$\dot{D}_{out}$	
Jordan					
	1044	2	8	483.87	[47]
	681	8	21	320.33	[5]
	799	9	147	380.70	[45]
Morocco					
	1600	20	10	751.70	[48]
	1700	30	10	803.94	[49]
	1340 ± 100	21 ± 2	32 ± 4	633.10	[8]
	1550 ± 150	25 ± 2	34 ± 4	732.62	[8]
	1200 ± 100	19 ± 2	33 ± 4	567.25	[8]

Table 5
Activity concentrations of radionuclides in, and associated external dose rates from NP fertilizer made from Jordanian and Moroccan PRs by dissolving in HNO_3.

Country	Activity concentration (Bq kg^{-1})			Dose rate (nGy h^{-1})	Reference
	^{226}Ra	^{232}Th	^{40}K	$\dot{D}_{out}$	
Pakistan	489 ± 2	29 ± 4	46 ± 9	245.35	[16]
Pakistan					
Mean	389.4	79.9	205.7	236.74	[50]
Minimum	207	14	129	109.47	
Maximum	501	163	298	342.34	
Romania	360	16.23			[2]
Italy	124 ± 11	2.9 ± 0.8	30 ± 3	60.29	[8]
Italy	131 ± 11	3.7 ± 1.4	25 ± 3	63.80	[8]

Table 6
Activity concentrations of radionuclides in, and associated external dose rates from PG waste from some countries of the world.

Country	Activity concentration (Bq kg^{-1})			Dose rate (nGy h^{-1})	Reference
	^{226}Ra	^{232}Th	^{40}K	$\dot{D}_{out}$	
Brazil/Tapira	180	206	60	210.09	[6]
Brazil/Tapira	169	185	63	192.45	[6]
Brazil/Catalão	292	172	53	241.00	[6]
Brazil/Catalão	292	151	48	228.11	[6]
Greece	585 ± 2	3.3 ± 0.1	13.0 ± 1.0	272.81	[7]
Greece	688 ± 9	2.7 ± 0.1	5.0 ± 0.4	319.70	[7]
Greece	626 ± 3	3.0 ± 0.5	5.0 ± 0.4	291.23	[7]
Spain	740 ± 60	<8	50 ± 6	348.80	[14]

Table 7
Activity concentration of radionuclides in, and associated dose rates from PF and PG from different countries of the world produced by dissolving PR in H_2SO_4.

Country	Activity concentration (Bq kg^{-1})			Dose rate (nGy h^{-1})	Reference
Material	^{226}Ra	^{232}Th	^{40}K	$\dot{D}_{out}$	
Bangladesh					[51]
PF (DAP)	98.6 ± 8.4	14.6 ± 2.4	74.2 ± 5.8	57.47	
PG	234 ± 12.8	20.8 ± 4.0	107.9 ± 8.7	125.17	
Brazil					[52]
PF (MAP)	5	221	5	136.00	
PG	280	206	60	256.29	
PG	269	185	63	238.65	
Brazil					[53]
PF (NPK)	13 ± 2	30 ± 3	8915 ± 445	395.88	
PF (NPK)	14 ± 2	31 ± 3	8935 ± 498	397.78	
PG	106 ± 9	153 ± 13	198 ± 18	149.64	
PG	137 ± 10	147 ± 11	169 ± 17	159.13	
Egypt					
PF	366 ± 10.5	66.7 ± 7.3	4 ± 2.6	209.55	[27]
PG	596 ± 25	6.2 ± 2.4	2.1 ± 0.4	279.18	[54]
Jordan					[5]
PF	37 ± 6	8 ± 2	38 ± 18	23.51	
PG	376 ± 62	4 ± 2	40 ± 32	177.80	

cement manufacturing, paints making, and filling of pores before painting in a house. The enhanced concentration of ^{226}Ra in the building materials containing PCC can lead to indoor external exposure to gamma rays and internal exposure to radon (^{222}Rn) in the houses. The mixing of PCC in building material enhances the activity concentration of ^{226}Ra in the material. Tahir et al. [25] have reported 42.1 ± 5.2, 52.3 ± 1.6, 945 ± 50 Bq kg^{-1} activity concentrations respectively of ^{226}Ra, ^{232}Th and ^{40}K in the soil (the basic constituent of bricks) of Multan district. Assuming that at the most 20% of the PCC can be mixed in 80% of the soil used to fabricate the bricks; therefore the activity concentrations of the radionuclides transferred into the bricks from the PCC and soil is in same proportion.

Indoor external dose $\dot{D}_{in}$ in a room containing PCC in bricks was calculated using Eq. (3) and is given in Table 1. The average value and the range of $\dot{D}_{in}$ in the room is 246 ± 17 (222–277) nGy h^{-1} and that in soil made room calculated from data given in Table 3 is 121 (49–240) nGy h^{-1}. The average value of $\dot{D}_{in}$ in a room containing PCC in soil bricks is about twice higher than that in the room constructed only of soil bricks. For 80% occupancy factor, annual effective dose due to indoor external exposure to gamma-ray was calculated using Eq. (7). The effective dose was 1.2 ± 0.1 (1.1–1.4) m Sv y^{-1}, which is higher than the annual limit of 1 m Sv recommended by ICRP [22] for the general public. Therefore, the material containing PCC should be monitored for radioactive content before its use as a building material. The value of $\dot{D}_{in}$ is higher than $\dot{D}_{out}$; the ratio $\dot{D}_{in}/\dot{D}_{out}$ in PCC waste varies from 1.34 to 2.15 with an average value of 1.7 (Table 1). Due to 80% indoor occupancy factor, the indoor effective dose E_{in} from PCC waste becomes 5–9 times higher than that of outdoor effective dose E_{out} where occupancy factor is 20%.

3.3. Environmental radioactive pollution

The PCC generated as a process waste at NP fertilizer plants being very fine grained therefore can have vast applications in industry, medicine and environment. A long list of different uses of PCC is available on internet [11]. According to Roskill [26], "world annual demand for PCC is forecast to grow by an average of 4% from around 13 Mt in 2007 to nearly 16 Mt by 2012. Growth rates will be highest in the paint (6% py) and rubber (4% py) industries though the largest increases in terms of tonnage will be in paper and paint. Much of the increase in demand will take place in Asia, especially in China, with much lower rates of growth forecast for North America and Europe. Asia's domination of the world PCC market is due both to recent growth in the regional paper and plastics industries, and to the smaller market share for fillers held by ground calcium carbonate (GCC) in China".

Table 8
Ultimate destination of the PCC generated at the NP fertilizer factory at Multan, Pakistan.

Activity	Consumption (%)
Formation of CAN fertilizer	50
Textile industry	1
Toothpaste and ceramic industry	1
Land amendments	8
Pileup waste (miscellaneous applications)	40

Radioactively contaminated PCC waste becomes a source of radioactive pollution in the environment. At Pak-Arab fertilizer factory in Pakistan, the stacks of the PCC are discharged directly on the earth surface, which therefore present radiological hazard of TENORM and heavy metals in the environment. The severity of the summer in Multan, generate dust storms mixed with the PCC that pollute the environment at large extent. In the rainy season, the suspended PCC and that in pileup are eroded and the water bodies are contaminated. Radioactivity and the heavy metals in the PCC, directly and indirectly, affect the human beings. The heritage of Multan is under threat due to the presence of NP fertilizer factory in the city. This is a major concern for the public authorities, who must carefully consider the environmental impact [27] of the of the NP fertilizer factory at Multan in Pakistan.

The intensity of the pollution depends on the type of practical applications of the TENORM containing PCC. Its commercial use can lead to dispersion of radioactivity in the environment. Different uses of the PCC can become the cause of radioactive pollution. The PCC waste generated at the understudy NP plant is mainly used as a feedstock for CAN in the fertilizer industry [23,28] and in agriculture for the soil amendment and stabilizing [6]. This material is also used in the construction industry and in cement production [17]. The use of this material in paper industry [29,30] and for health and dietary uses have also been reported [31]. The proportion of the PCC generated at Pak-Arab fertilizer factory at Multan in Pakistan, used in main activities is given in Table 8.

The potential uses of the understudy PCC waste include the manufacture of adhesives, chalks, chemicals, cosmetics, dentifrice, diapers, fillers, food supplement, glass, inks, paints, pharmaceuticals, plastics, putties, rubber, sealants, toothpaste, tooth powder, varnishes, etc. Calcium carbonate can be used: in the treatment of drinking water, to neutralize acidic conditions in soil and water;

as primary component of garden lime, also known as agricultural lime; and in de-sulphurisation of flue gas and waste water treatments [32,33]. The use of this material in garden may become a source of internal and external exposure of the people to radiation. The TENORM in the PCC waste will be the source of radioactive pollution in the environment.

4. Conclusions

The NORM in phosphate rock (PR) is transferred as TENORM to the precipitated calcium carbonate (PCC), the waste of NP factory at Multan in Pakistan, which contained enhanced activity concentrations of ^{226}Ra than that of ^{40}K, and ^{232}Th due to the alliance of uranium with PR. The concentration level of ^{226}Ra in the PPC as TENORM was higher than that in naturally occurring limestone and marble, and in the worldwide soil. It was comparable to that in the Italian PCC waste, while lower than that in the PCC waste generated at Romania. The variation of TENORM in the worldwide waste from NP fertilizer plants may be the different geological origins of PR used for the manufacture of the fertilizer.

Radiological hazard of the TENORM in the PCC was assessed on the basis of indoor and outdoor external radiation absorbed dose rates. The outdoor dose rate from the PCC was higher than that from limestone and marble, and the worldwide background level of soil. It was lower than that in the PCC waste from some countries in comparison. The understudy PCC is not a radiological threat as far as outdoor external exposure is concerned because annual effective dose is much lower than the limit of 1 m Sv per year for the general public. The dose rate is further reduced after the dilution of the PCC concentration in agricultural fields. The 20% mixing of PCC in building bricks increases the indoor annual effective dose beyond the limit of 1 m Sv for general public. Potential radiological hazards associated with various applications of the PCC are not that much to restrict its commercial use.

Record of radionuclides activity concentrations in PR, PF and PCC, and the concentration of radon in the warehouses should be maintained regularly at the understudy fertilizer factory of Pakistan. The effect of the pollutants of NP factory on the historical building of Multan should be evaluated. For the management of radioactive PCC waste, the nuclear waste regulatory authority of the country should be involved. To minimize the problem created with the PCC production, it is suggested that the PCC generation should be reduced; furthermore radioactive and non-radioactive heavy metals should be removed at the stage of dissolution of PR in acid before the process of fertilizer production.

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